

Activated Dynamics and the Ergodic-Nonergodic Transition

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The hindered diffusion model is introduced. It is a continuum model giving the dynamics of a conserved density. Similar to the spin-facilitated models, the kinetics are hindered by a fluctuating diffusion coefficient that decreases as the local density approaches some geometrically constrained value where the mobility goes to zero. The model leads in a natural way to activated dynamics at low temperatures and high densities. In a well defined approximation the theory is shown to be compatible with mode-coupling theory. Indeed in the simplest form of the model we find an ergodic-nonergodic transition into a phase that supports activated kinetics and nonergodic behavior.

We introduce a simple model for the structural glass transition that naturally leads to activated dynamics at low temperature and high densities. This model is continuum generalization of the spin-facilitated (SF) dynamics¹⁻⁴ that have been put forth as models for glassy dynamics. It is more physical than the SF models since it is formulated in terms of a density field ρ that is conserved. As in the SF models, the equilibrium static behavior can be chosen to be noninteracting. In the continuum description this corresponds to choosing Gaussian static statistics. The model can also be used to make contact with mode-coupling theory^{5,6}. The key new ingredient in this approach is to choose a bare diffusion coefficient⁷ that is density dependent $D(\rho)$. Technically this complicates the problem compared to the simplest field theoretical models that have been proposed^{8,9}. This is because we must treat multiplicative noise. Generally this has been a difficult proposition. However, there are certain constrained models, typically with conservation laws, where the treatment^{10,11} of multiplicative noise is tractable. The general class of models includes those discussed by Dean¹², Kawasaki and Miyazima¹³, and Miyasaki and Reichmann¹⁴. The important difference is that they deal with a bare diffusion coefficient that is linear in the density. We study here the situation where there is a high density constraint on the bare diffusion coefficient.

The model we study here is given in Langevin equation language by

$$\frac{\partial \rho}{\partial t} = \vec{\nabla} \cdot \left(D(\rho) \vec{\nabla} \frac{\delta \mathcal{H}_\rho}{\delta \rho} \right) + \vec{\nabla} \cdot (g_\rho \vec{\eta})$$

where $D(\rho)$ is the bare diffusion coefficient defined below, $\vec{\eta}$ is Gaussian-white noise with variance

$$\langle \eta_\alpha(\mathbf{x}, t) \eta_\gamma(\mathbf{y}, t') \rangle = 2k_B T D_0 \delta_{\alpha\gamma} \delta(\mathbf{x} - \mathbf{y}) \delta(t - t') \quad , \quad (1)$$

the multiplier $g_\rho = \sqrt{\frac{D(\rho)}{D_0}}$ and the effective Hamiltonian \mathcal{H}_ρ can be taken to be quadratic in ρ :

$$\mathcal{H}_\rho = \int d^d x_1 d^d x_2 \frac{1}{2} \delta \rho(\mathbf{x}_1) \chi^{-1}(\mathbf{x}_1 - \mathbf{x}_2) \delta \rho(\mathbf{x}_2)$$

where $\delta \rho(\mathbf{x}_1) = \rho(\mathbf{x}_1) - \rho_0$.

The field theoretic version of this model corresponds to the MSR¹⁵ action given by

$$A = \int d^d x dt \left[D(\rho) (\nabla \hat{\rho})^2 + i \hat{\rho} \left[\dot{\rho} - \sum_i \nabla_i \left(D(\rho) \nabla_i \frac{\delta \mathcal{H}_\rho}{\delta \rho} \right) \right] \right]$$

where $\hat{\rho}$ is the usual field conjugate to ρ . The theory from this point of view will be discussed elsewhere.

We will analyze this problem using the Fokker-Planck (FP) formalism¹⁶. In this approach the density time correlation function is given by

$$C(\mathbf{x}_1 - \mathbf{x}_2, t) = \langle \delta \rho(\mathbf{x}_2) e^{-\tilde{D}_\rho t} \delta \rho(\mathbf{x}_1) \rangle$$

where the average is an equilibrium average over the static distribution $e^{-\beta \mathcal{H}_\rho} / Z$ and the adjoint FP operator is defined by

$$\tilde{D}_\rho = \int d^d x \int d^d y \left[\frac{\delta \mathcal{H}_\rho}{\delta \rho(\mathbf{x})} - k_B T \frac{\delta}{\delta \rho(\mathbf{x})} \right] \Gamma_\rho(\mathbf{x}, \mathbf{y}) \frac{\delta}{\delta \rho(\mathbf{y})} \quad .$$

where

$$\Gamma_\rho(\mathbf{x}, \mathbf{y}) = \nabla_x \cdot \nabla_y (D(\rho(\mathbf{x})) \delta(\mathbf{x} - \mathbf{y})) \quad .$$

It is technically important¹⁷ that

$$\int d^d z \frac{\delta}{\delta \rho(\mathbf{z})} \Gamma_\rho(\mathbf{z}, \mathbf{x}) = 0 \quad .$$

We study a model with a simple physical choice for $D(\rho)$:

$$D(\rho) = D_0 \theta(\rho_c - \rho) \frac{(\rho_c - \rho)}{\rho_c} \quad (2)$$

where D_0 , introduced in Eq.(1), and ρ_c are positive parameters. This form reflects the geometrical fact that

as the density increases it is more difficult for particles to move and there is some local density ρ_c above which a particle is stuck. This is physically similar to spin-facilitated models where mobility is diminished if the local environment is blocked. We call this model the hindered diffusion model. More realistic models involve putting in more static structure and coupling the density to the other slow variables¹⁸ in the system.

In order to treat the high density constraint adequately we have organized the theory using the memory function formalism developed in Refs. 19 and 20. The Laplace-Fourier transform,

$$C(k, z) = -i \int_0^\infty e^{izt} \int d^d x_1 e^{i\mathbf{k} \cdot (\mathbf{x}_1 - \mathbf{x}_2)} C(\mathbf{x}_1 - \mathbf{x}_2, t) \quad , \quad (3)$$

satisfies the kinetic equation

$$[z + K(k, z)]C(k, z) = \tilde{C}(k) \quad (4)$$

where $\tilde{C}(k) = k_B T \chi(k)$ is the static density correlation function and $K(k, z) = K^{(s)}(k) + K^{(d)}(k, z)$ is the memory function. We consider first the approximation where we keep only the static part of the memory function: $K^{(s)}$. Formally $K^{(s)}$ is of order D_0 while the dynamic part $K^{(d)}(k, z)$ is of order D_0^2 . We will discuss approximations for $K^{(d)}$, including mode coupling contributions, later.

The static part of the memory function is given, without approximation, by

$$K^{(s)}(k) = i\beta^{-1} k^2 \bar{D} \tilde{C}^{-1}(k) = ik^2 \bar{D} \chi^{-1}(k) \equiv i\Gamma_0(k) \quad . \quad (5)$$

where $\bar{D} = \langle D(\rho) \rangle$ is the average diffusion coefficient. If $\rho_0 = \langle \rho \rangle$ is the average uniform density and $S = \langle (\delta\rho)^2 \rangle$, then, because the static fluctuations are Gaussian, we must have for the singlet probability distribution

$$P[\sigma] = \langle \delta(\sigma - \rho(1)) \rangle = \frac{e^{-\frac{1}{2S}(\rho_0 - \sigma)^2}}{\sqrt{2\pi S}} \quad . \quad (6)$$

The parameter S is related to the static structure factor by

$$S = \int \frac{d^d k}{(2\pi)^d} k_B T \chi(k) \quad (7)$$

and S is proportional to the temperature. The average diffusion coefficient can be evaluated as

$$\bar{D} = \frac{\rho_0 D_0}{\rho_c \epsilon_0 2\sqrt{\pi}} \left[\sqrt{\pi} \epsilon (erf(\epsilon) + erf(\epsilon_0)) + e^{-\epsilon^2} - e^{-\epsilon_0^2} \right] \quad (8)$$

where we have introduced the dimensionless parameters $\epsilon = \frac{(\rho_c - \rho_0)}{\sqrt{2S}} \approx 1/\sqrt{T}$ and $\epsilon_0 = \frac{\rho_0}{\sqrt{2S}}$. In the high density $\epsilon < 0$, low temperature limit $|\epsilon|$ and ϵ_0 are both large and we find that the physical diffusion coefficient is activated in temperature:

$$\bar{D} = D_0 \frac{\rho_0}{\rho_c} \frac{1}{2\sqrt{\pi}\epsilon_0} e^{-\epsilon^2} \left(\frac{1}{2\epsilon^2} - \frac{3}{4\epsilon^4} + \dots \right) \quad . \quad (9)$$

The activated dynamics results from the fact that if $\rho_0 > \rho_c$, then one can have motion only if there is a local fluctuation where $\rho < \rho_c$. At low temperatures such fluctuations will be rare.

Putting Eq.(5) back into Eq.(4), assuming $K = K^{(s)}$, and inverting the Laplace transform gives

$$C(k, t) = e^{-k^2 \bar{D} \chi^{-1}(k)t} \tilde{C}(k) = e^{-\Gamma_0(k)t} \tilde{C}(k) \quad . \quad (10)$$

One has dramatic slowing down for $\epsilon < 0$ and large.

The dynamic part of the memory function is the sum of two pieces:

$$K^{(d)}(q, z) \tilde{C}(q) = \Gamma^{(d)}(q; z) = \bar{\Gamma}(q; z) + \Gamma_{sub}(q; z).$$

In coordinate space, the first piece is given by

$$\bar{\Gamma}(\mathbf{x}_1 - \mathbf{x}_2; z) = -\langle v(\mathbf{x}_2) R(z) v(\mathbf{x}_1) \rangle \quad (11)$$

where the *current* is defined by $v(\mathbf{x}_1) = i\bar{D}_\rho \rho(\mathbf{x}_1)$ and $R(z) = [z + i\bar{D}_\rho]^{-1}$ is the resolvent operator. The Fourier transform of the second term, the *subtraction* part, is given by

$$\Gamma_{sub}(\mathbf{q}; z) = \langle v_{-\mathbf{q}} R(z) \rho_{\mathbf{q}} \rangle C^{-1}(\mathbf{q}; z) \langle \rho_{-\mathbf{q}} R(z) v_{\mathbf{q}} \rangle \quad . \quad (12)$$

In carrying out the designated averages it is useful to write the current in the form

$$v(1) = -i \sum_{\alpha_1} \nabla_{x_1}^{\alpha_1} \int d\sigma D(\sigma) g_\sigma(1) \tilde{\rho}(1) \quad . \quad (13)$$

where $g_\sigma(1) = \delta(\sigma - \rho(1))$ and we have introduced the field

$$\tilde{\rho}(1) = \tilde{\rho}_{\alpha_1}(\mathbf{x}_1, t_1) = \nabla_{x_1}^{\alpha_1} \int d^d x_2 \chi^{-1}(\mathbf{x}_1 - \mathbf{x}_2) \rho(\mathbf{x}_2, t_1) \quad .$$

In evaluating $\Gamma^{(d)}$ we make the simplest approximation. We assume that the fields ρ appearing in the averages in Eqs.(11) and (12), can be treated as Gaussian. Corrections to this approximation will be discussed elsewhere. We need, in the coordinate and time regime, the notation

$$C(12) = \langle \delta\rho(1) \delta\rho(2) \rangle$$

$$C(1\alpha_1, 2) = \langle \tilde{\rho}(1) \delta\rho(2) \rangle$$

$$C(1\alpha_1, 2\alpha_2) = \langle \tilde{\rho}(1) \tilde{\rho}(2) \rangle$$

After doing the Gaussian averages, the subtraction term, Eq.(12), is given by

$$\Gamma_{sub}(\mathbf{x}_1 - \mathbf{x}_2; z) = - \sum_{\alpha_1 \alpha_2} \nabla_{x_2}^{\alpha_2} \nabla_{x_1}^{\alpha_1} C(\mathbf{x}_1 \alpha_1, \mathbf{x}_2 \alpha_2; z) \bar{D}^2 \quad .$$

The more complicated contribution to the dynamic part of the memory function and is given, in the time regime,

by $\bar{\Gamma}(12) = -\langle v(2)v(1) \rangle$. After carrying out the average we find

$$\bar{\Gamma}(12) = \sum_{\alpha_1 \alpha_2} \nabla_{x_1}^{\alpha_1} \nabla_{x_2}^{\alpha_2} \left[C(1\alpha_1, 2\alpha_2) + C(1\alpha_1, 2)C(2\alpha_2, 1) \frac{\partial}{\partial C(12)} \right] W(12) \quad (14)$$

where $W(12)$ is the diffusion-diffusion correlation function that has the power-series representation

$$W(12) = \langle D(1)D(2) \rangle = \sum_{\ell=0}^{\infty} \frac{(C(12))^\ell}{\ell!} \bar{D}_\ell^2 \quad (15)$$

where we have introduced the average of the derivatives of the bare diffusion coefficient:

$$\bar{D}_\ell = \int d\sigma_1 P[\sigma_1] \frac{\partial^\ell}{\partial \sigma_1^\ell} D(\sigma_1) \quad (16)$$

It is convenient to break $W(12)$ into three pieces

$$W(12) = \bar{D}^2 + \bar{D}_1^2 C(12) + \left(\frac{D_0}{\rho_c} \right)^2 \frac{S}{2\pi} \tilde{W}(f) \quad (17)$$

where the remaining sum given by $\tilde{W}(f)$ can be rewritten as an integral

$$\tilde{W}(f) = \int_0^{\sin^{-1} f} dz (f - \sin z) e^{-\frac{2z^2}{(1+\sin z)}} \quad (18)$$

where $f(12) = C(12)/S$.

We can associate distinct terms in $\Gamma^{(d)}$ with the three terms in $W(12)$ given in Eq.(17). The \bar{D}^2 term can be shown to be equal to $-\bar{\Gamma}_{sub}(12)$ and cancels the subtraction. The \bar{D}_1^2 term gives

$$\Gamma_{MC}^{(d)}(q, t) = \frac{\bar{D}_1^2}{2} \int \frac{d^d k}{(2\pi)^d} C(\mathbf{k}, t) C(\mathbf{q} - \mathbf{k}, t) [\mathbf{q} \cdot [\mathbf{k} \chi^{-1}(k) + (\mathbf{q} - \mathbf{k}) \chi^{-1}(\mathbf{q} - \mathbf{k})]]^2 \quad (19)$$

and we have the standard mode-coupling contribution. The term proportional to \tilde{W} in $W(12)$ gives rise to the contribution

$$\Gamma_{BMC}^{(d)}(\mathbf{q}, t) = q^2 \int \frac{d^d k}{(2\pi)^d} \left(\frac{D_0}{\rho_c} \right)^2 \frac{S^2}{2\pi} \times \chi^{-2}(k) \mathbf{k} \cdot \mathbf{q} f(k, t) \tilde{W}(\mathbf{q} - \mathbf{k}) - \left(\frac{D_0}{\rho_c} \right)^2 \frac{S^2}{2\pi} \int \frac{d^d k_1}{(2\pi)^d} \frac{d^d k_2}{(2\pi)^d} \frac{d^d k_3}{(2\pi)^d} \tilde{W}'(k_3) f(k_1, t) f(k_2, t)$$

$$\times \delta(\mathbf{q} - \mathbf{k}_1 - \mathbf{k}_2 - \mathbf{k}_3) \mathbf{k}_1 \cdot \mathbf{q} \mathbf{k}_2 \cdot \mathbf{q} \frac{1}{2} (\chi^{-1}(k_2) - \chi^{-1}(k_1))^2$$

where $\tilde{W}(k)$ is the Fourier transform of $\tilde{W}(f)$ given by Eq.(18) and $\tilde{W}'(k)$ is the Fourier transform of $\frac{\partial}{\partial f} \tilde{W}(f)$. The dynamic part of the memory function is given by $K^{(d)}(q, t) = \Gamma^{(d)}(q, t)/\tilde{C}(q)$ and the static part by Eq.(5). These results go back into the kinetic equation given by Eq.(4). It turns out that we need to make some additional manipulations before looking for a solution for $C(q, t)$.

If we take the inverse Laplace transform of the kinetic Eq(4), we find

$$\dot{C}(t) - iK^{(s)}C(t) - \int_0^t ds K^{(d)}(t-s)C(s) = 0 \quad (20)$$

It is easy to see that Eq.(20) with $K^{(d)}(t)$ given by $\Gamma^{(d)}(t)/\tilde{C}$, does not lead to an ergodic-nonergodic transition, instead numerical solutions blow up. Kawasaki²¹ suggested that the kinetic equation, Eq.(4), be rewritten in the form

$$\left(z + \frac{K^{(s)}}{1 + K^{(s)}N(z)} \right) C(z) = \tilde{C} \quad (21)$$

Comparing with Eq.(4) we can solve for $N(z)$ to obtain

$$N(z) = -\frac{K^{(d)}(z)}{K^{(s)}(K^{(s)} + K^{(d)}(z))} \quad (22)$$

In a perturbation theory calculation where we treat $K^{(d)}(z)$ as small we have

$$N(z) = -\frac{K^{(d)}(z)}{(K^{(s)})^2} \quad (23)$$

So $N(z)$ can be determined using perturbation theory. Next we note that Eq.(21) can be written in the form

$$(1 + K^{(s)}N(z))(zC(z) - \tilde{C}) + K^{(s)}C(z) = 0 \quad (24)$$

Taking the inverse Laplace transform gives

$$\dot{C}(t) = -\Gamma_0 C(t) - \Gamma_0 \int_0^t ds N(t-s) \dot{C}(s) \quad (25)$$

where $\Gamma_0 = -iK^{(s)}$ sets the time scale. This equation produces a nonergodic phase for the standard mode coupling kernel.

The last step in determining $N(q, t)$ is to choose the static correlation function $\tilde{C}(q)$. The simplest assumption is that the static correlation function is a constant up to a cutoff: $\chi(q) = \frac{1}{r}$ for $q < \Lambda$ and zero for larger wavenumbers. In this case we have

$$\Gamma^{(d)}(q, t) = \frac{\bar{D}_1^2}{2} (rq^2)^2 S^2 \int_{\Lambda} \frac{d^d k}{(2\pi)^d} f(k, t) f(\mathbf{q} - \mathbf{k}, t)$$

$$+ \frac{(qr)^2}{2\pi} \left(\frac{D_0}{\rho_c} \right)^2 S^2 \int_{\Lambda} \frac{d^d k}{(2\pi)^d} \mathbf{k} \cdot \mathbf{q} f(k, t) \tilde{W}(\mathbf{q} - \mathbf{k}, t) \quad (26)$$

where $f(k, t)$ is the Fourier transform of $f(r, t) = C(r, t)/S$. $\Gamma^{(d)}(q, t)$ is related to $N(q, t)$ by Eq.(23), which takes the form:

$$N(q, t) = \frac{\Gamma^{(d)}(q, t)}{q^4 \bar{D}^2 r^2 \bar{C}} = g_0 I_{MC}(q, t) + g_1 I_{BMC}(q, t) \quad (27)$$

where in three dimensions the couplings are given by

$$g_0 = \frac{2\pi S^2}{\bar{C}} \left(\frac{\bar{D}_1}{\bar{D}} \right)^2 \quad ; g_1 = \frac{4\pi S^3}{\bar{C}} \left(\frac{\bar{D}_2}{\bar{D}} \right)^2 .$$

The functions $I_{MC}(q, t)$ and $I_{BMC}(q, t)$ follow from Eqs.(26) and (27) and the definitions of g_0 and g_1 . Because of the ratios of \bar{D}_ℓ the g 's are not activated in temperature.

The set of equations to be solved, Eqs.(25) and (27), is governed by the parameters ρ_c , ρ_0 , S and the wavenumber cutoff Λ . The static correlation function can be written as $\tilde{C}(q) = 6\pi^2 S/\Lambda^3$, which follows from Eq.(7). Time is measured in units of $(\bar{D}r)^{-1}$.

In the dense frozen region where $\epsilon < 0$ and is large in magnitude we have $g_0 = \frac{2\Lambda^3 \epsilon^2}{3\pi}$ and $g_1 = \frac{8\Lambda^3 \epsilon^4}{3\pi}$, which suggests that for large ϵ there will be an ergodic-nonergodic transition.

We solved the coupled set of equations numerically. Let us first fix $\rho_c = 1.0$ and the momentum cutoff $\Lambda = 1.0$ and look at solutions $C(q, t)$. If we begin with $\rho_0 = 0.5$ and $S = 0.1$ we find that $C(q, t)$ decays exponentially with a decay rate, because of the conservation law, proportional to q^2 . Thus the kinetics are less sensitive to the cutoff as time evolves. If we increase S to 0.2 we see little change in the dynamics. However, it is easy to see that the couplings g_0 and g_1 increase with S . While the model is only physically applicable²² to structural glasses for small S , we can look at solutions for larger S and we find an ergodic-nonergodic transition (ENE) along the line $S_H = A_H(\rho_H - \rho_0)^{1/3}$ where $A_H = 2.25$ and $\rho_H = 2.78$. This holds even for $\rho_0 > \rho_c$.

In the dense regime $\rho_0 > \rho_c$ $\epsilon < 0$ we find a line of ENE transitions for small values of S satisfying the relationship $S = A(\rho_0 - \rho_c)^2$ with a good fit for $A = 0.245$. Thus there is a regime where we simultaneously have activated dynamics and a nonergodic phase. As ρ_0 increases beyond ρ_c , there is a value of $\rho_0 \approx \rho_H$ where the high S nonergodic branch meets the low S branch and for higher ρ_0 all states are nonergodic. One can look at the kinetics in the nonergodic regime and obtain a good fit to $C(q, t)/\tilde{C}(q) = f(q) + A_q/t$. The ENE phase separation curves are determined by fitting to this form and choosing for fixed ρ_0 and $q = 0.4$ that value of S that gives $f(q = 0.4) = 0.5$.

Similar behavior is found for other choices of ρ_c and wavenumbers.

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